CHEMICAL MECHANICAL POLISHING SLURRY FOR RUTHENIUM TITANIUM NITRIDE AND POLISHING PROCESS USING THE SAME

BACKGROUND

Technical Field

A chemical mechanical polishing (abbreviated as 'CMP') slurry for ruthenium titanium nitride (abbreviated as 'RTN'), and a polishing process using the same are disclosed. In particular, a slurry is disclosed that is used when a RTN film deposited as a barrier film is polished according to a CMP process in forming a capacitor using a $(Ba_{1-x}Sr_x)TiO_3$ (abbreviated as 'BST') film as a dielectric film in a process technology below 0.1μm. A polishing process using the same is also disclosed.

Description of the Related Art

RTN is a precious material which has excellent mechanical and chemical properties and which is essential to form a high performance capacitor. RTN is used as a barrier film. According to the present invention, a CMP process is employed to polish RTN.

Here, the CMP process is a purification process mostly used for a semiconductor wafer manufacturing process over 64M requiring high accuracy, and the slurry is a chemicals for planarizing various insulating films on a silicon substrate. In general, the slurry consists

of a solvent, a compound and an abrasive. Mostly, a surfactant is added in a small volume to improve a CMP property.

A compound and an abrasive are dependent upon a kind of a film to be polished. For example, an alkali solution such as KOH or NH_4OH is used as a compound for polishing an oxide film, and SiO_2 is used as an abrasive for polishing the oxide film, and an oxidizer such as hydrogen peroxide is used as a compound for polishing a metal film, H_2SO_4, HNO_3 or HCl is added in a small volume to adjust the slurry to acidity, and Al_2O_3 is used as an abrasive for polishing the metal film.

The CMP process is performed by combining a chemical reaction and a mechanical reaction. The chemical reaction implies a chemical reaction between a compound contained in the slurry and a film. In the mechanical reaction, a force applied by a polishing device is transmitted to the abrasive in the slurry, and the film receiving the chemical reaction is mechanically separated by the abrasive.

That is, in the CMP process, a rotating polishing pad and a substrate are directly pressure-contacted, and the polishing slurry is provided to an interface thereof. Thus, the surface of the substrate is mechanically chemically polished and planarized by the polishing pad coated with the slurry. Accordingly, a polishing speed

and a defect and erosion of the polished surface vary with a composition of the slurry.

An appropriate slurry is not provided in polishing RTN according to the CMP process, and thus a slurry for tungsten or aluminum is employed. In this case, the polishing speed of RTN is very low, and thus the CMP process is performed for a long time under a high polishing pressure. Therefore, scratches and impurities are seriously generated on an insulating film.

And because RTN must be polished for a long time under a high polishing pressure, dishing which is polished more than the peripheral insulating film and erosion are generated on RTN adjacent to the insulating film, which deteriorate the properties of the device.

It will now be explained in detail with reference to the accompanying drawings.

Figure 1 is a cross-sectional view illustrating a semiconductor device where RTN is deposited as a barrier film. A gate oxide film 2, a gate electrode 3 and a mask insulating film 4 are formed on a semiconductor substrate 1. An oxide film spacer 5 is formed at the side walls of the resultant structure. An interlayer insulating film is formed over the resultant structure. A presumed capacitor contact region is removed according to a photolithography process, thereby forming a interlayer insulating film pattern 6.

Thereafter, a stacked layer of polysilicon 7 and buffer film 8 fills up the contact hole as a contact plug and a RTN thin film 9 is formed on the whole surface of the resultant structure. A RTN thin film 9 is patterned and planarized according to the CMP process, thereby forming a barrier film.

Figure 2 is a cross-sectional view in a state where the CMP process is performed on the RTN thin film 9 of Figure 1 by using the general slurry.

The general conditions of the CMP process include a polishing pressure of 4 to 7psi, a table revolution number of 80 to 100 rpm by a rotary type system, and a table movement speed of 600 to 700 ft/min by a linear type system.

However, the polishing speed of RTN is very low under the general conditions, and thus the CMP process is not successfully performed. So as to increase the polishing speed of RTN, the CMP process should be performed for an extended period of time, increasing a supply amount of slurry and a polishing pressure.

As a result, as shown in Figure 2, scratches 10 are generated on the interlayer insulating film pattern 6 due to the high polishing pressure, impurities such as slurry residuals or particles 11 remain thereon, the RTN thin film 9 is polished more than the interlayer insulating film from a time of exposing the interlayer insulating

film to cause a dishing phenomenon, and the peripheral interlayer insulating film is seriously eroded. Moreover, a slurry for the interlayer insulating film is required to remove the scratches 10 and the particles 11 generated after the CMP process of the RTN thin film.

That is, the RTN thin film 9 is polished in a first step, and the surface of the interlayer insulating film pattern 6 is slightly polished by using a specific slurry in a second step, thereby preventing generation of the particles 11.

SUMMARY OF THE DISCLOSURE

Accordingly, a CMP slurry and a CMP process using the same are disclosed which can improve a polishing speed of RTN under a low polishing pressure and polish RTN according to an one-step process by using one kind of slurry.

In addition, a method for manufacturing a semiconductor device according to a CMP process using a slurry, and a semiconductor device manufactured according to the method are also disclosed.

More specifically, a CMP slurry for RTN, containing ceric ammonium nitrate [$(NH_4)_2Ce(NO_3)_6$], a CMP process using the same, a method for manufacturing a semiconductor device according to the CMP process using

the slurry, and a semiconductor device manufactured according to the method are disclosed.

BRIEF DESCRIPTION OF THE DRAWINGS

The disclosed slurries, processes, methods and devices will be better understood with reference to the accompanying drawings which are given only by way of illustration and thus are not limitative, wherein:

Figure 1 is a cross-sectional view illustrating a semiconductor device where a RTN is deposited as a barrier film;

Figure 2 is a cross-sectional view illustrating a semiconductor device where a RTN is patterned by using a known slurry; and

Figure 3 is a cross-sectional view illustrating a semiconductor device where a RTN is patterned by using a disclosed slurry.

DETAILED DESCRIPTION OF THE PRESENTLY PREFERRED EMBODIMENTS

First of all, a disclosed CMP slurry for RTN contains ceric ammonium nitrate [$(NH_4)_2Ce(NO_3)_6$]. The CMP slurry for RTN comprises distilled water, nitric acid (HNO_3), ceric ammonium nitrate and an abrasive. Preferably, HNO_3 is used in an amount ranging from about 1 to about 10% by weight of the slurry, ceric ammonium

nitrate is used in an amount ranging from about 1 to about 10% by weight of the slurry, and the abrasive is used in an amount ranging from about 1 to about 5% by weight of the slurry. Here, HNO_3 and ceric ammonium nitrate are used in an amount ranging from about 1 to about 10% by weight of the slurry, thereby stabilizing and easily handling the slurry.

HNO_3 maintains pH of the slurry ranging from about 1 to about 7, preferably from about 1 to about 3 for strong acidity. H_2SO_4, HCl or H_3PO_4 may be used instead of HNO_3. However, HNO_3 is most efficient.

Ceric ammonium nitrate serves as an oxidizer for extracting electrons from ruthenium atoms. The more HNO_3 and ceric ammonium nitrate are used, the more the polishing speed of RTN can be increased under the identical pressure.

In more detail, the slurry containing about 2wt% of HNO_3 and about 2wt% of ceric ammonium nitrate has a polishing speed of about 450 Å/min under a polishing pressure of about 1psi; the slurry containing about 2wt% of HNO_3 and about 6wt% of ceric ammonium nitrate has a polishing speed of about 700 Å/min under a polishing pressure of about 1psi; the slurry containing about 2wt% of HNO_3 and about 10wt% of ceric ammonium nitrate has a polishing speed of about 950 Å/min under a polishing pressure of about 1psi; the slurry containing about 6wt%

of HNO_3 and about 2wt% of ceric ammonium nitrate has a polishing speed of about 550 Å/min under a polishing pressure of about 1psi; and the slurry containing about 10wt% of HNO_3 and about 2wt% of ceric ammonium nitrate has a polishing speed of about 650 Å/min under a polishing pressure of about 1psi.

As compared with the fact that the slurry containing about 2wt% of HNO_3 and about 2wt% of ceric ammonium nitrate has a polishing speed of about 1000 Å/min under a polishing pressure of about 4psi, a polishing speed over 1000 Å/min even under a polishing pressure of about 1psi can be obtained, by slightly increasing a content of HNO_3 and ceric ammonium nitrate.

However, when HNO_3 and ceric ammonium nitrate are used in an amount over 10% by weight of the slurry, the slurry is not stabilized, and a polishing property of a pattern wafer is deteriorated. Accordingly, the content of HNO_3 and ceric ammonium nitrate should be maintained to a range from about 1 to about 10% by weight of the slurry. In addition, the process should be performed under a low polishing pressure to improve the polishing property of the pattern wafer.

The abrasive is used to improve a mechanical operation of the slurry. In the present invention, CeO_2, ZrO_2 or Al_2O_3 having a grain size below 1μm is used as the abrasive to minimize scratches.

Moreover, the slurry of the present invention contains a buffer solution to constantly maintain pH. Here, a mixture of organic acid and organic acid salt (1:1), preferably acetic acid and acetic acid salt (1:1) is used as the buffer solution.

As described above, the slurry of the present invention has strong acidity and reduces adhesion and density of ruthenium atoms by eroding or melting the surface of RTN. Therefore, a chemical property of RTN is so varied that RTN can be easily polished according to the CMP process.

That is, a mixture of HNO_3 and ceric ammonium nitrate added in the slurry increases an erosion and melting speed of RTN, to improve the polishing speed of RTN.

A method for preparing the CMP slurry for RTN in accordance with the present invention will now be described.

CeO_2, ZrO_2 or Al_2O_3 which is an abrasive is added to distilled water. Here, CeO_2, ZrO_2 or Al_2O_3 is added in a stirring speed of about 10000 rpm so that abrasive particles can not be agglomerated. Thereafter, HNO_3 and ceric ammonium nitrate are added thereto. The resulting mixture is stirred for about 30 minutes so that it can be completely mixed and stabilized. Therefore, the slurry of the present invention is prepared. Here, the abrasive is

used in an amount ranging from about 1 to about 5% by weight of the slurry, and HNO_3 and ceric ammonium nitrate are used in an amount ranging from about 1 to about 10% by weight of the slurry.

In addition, another aspect of the present invention provides a CMP process using the CMP slurry for RTN.

A method for forming a RTN pattern includes:

(a) preparing a semiconductor substrate where a RTN thin film is formed; and

(b) patterning the RTN thin film according to the CMP process using the CMP slurry composition for RTN.

A method for forming the pattern of the RTN thin film will now be explained in more detail. The semiconductor substrate where the RTN thin film is formed is pressure-adhered to a polishing pad formed on a rotary table of a CMP system. The slurry is supplied to an interface of the polishing pad and the RTN thin film, thus performing the CMP process. In the CMP process, a polishing pressure ranges from about 1 to about 4psi, a table revolution number of a rotary type system ranges from about 10 to about 80 rpm, and a table movement speed of a linear type system ranges from about 100 to about 600 ft/min in consideration of the polishing speed of RTN thin film and the polishing property of the interlayer insulating film and the pattern wafer. An end-point

detector is used to sense a time point of exposing the interlayer insulating film.

The exposure time of the interlayer insulating film is sensed by using the end-point detector, and thus the RTN thin film is not more polished than the interlayer insulating film, thereby preventing the dishing phenomenon and the erosion of the peripheral interlayer insulating film.

A semiconductor device where RTN is patterned by using the CMP slurry for RTN will now be explained with reference to the accompanying drawings.

Figure 3 is a cross-sectional view illustrating the semiconductor device where RTN is patterned by using the slurry of the present invention. The CMP process is performed on the RTN thin film 9 of Figure 1, by employing the slurry of the present invention.

Referring to Figure 3, when the CMP process is carried out in the process conditions of the present invention, defect generation on the interlayer insulating film pattern 6 and separation of the RTN thin film 9 are prevented to improve the polishing property.

That is, when the CMP process is performed under a minimum polishing pressure ranging from about 1 to about 4psi which is generally allowable in any system, the RTN thin film 9 is closely adhered to the interlayer

insulating film pattern 6, and defects and scratches are prevented.

In addition, when RTN thin film 9 is polished according to the CMP process using the slurry of the present invention, a slurry for the interlayer insulating film is not required, and RTN thin film 9 is polished according to an one-step process.

A method for manufacturing a semiconductor device includes patterning RTN by using the CMP slurry for RTN. The method for manufacturing the semiconductor device comprises:

(a) forming an interlayer insulating film on a semiconductor substrate 1 having a predetermined lower structure 2, 3, 4 and 5;

(b) patterning the interlayer insulating film to form an interlayer insulating film pattern 6 having a contact hole;

(c) filling up the contact hole with conducting material and performing over-etch to form a recess contact plug;

(d) depositing a RTN thin film 9 on the whole surface of the resultant structure; and

(e) forming a RTN thin film pattern on the recess contact plug by performing a CMP process.

As illustrated in Figure 3, a gate oxide film 2, a gate electrode 3 and a mask insulating film 4 are formed

on the semiconductor substrate 1 having the predetermined lower structure in step (a), an oxide film spacer 5 is formed at the sidewalls of the resultant structure and the conducting material of step (c) is polysilicon 8.

The method further comprises forming silicon nitride on the interlayer insulating film at the step (a) and forming a buffer film 8 between the contact plug and RTN film pattern. Preferably, the buffer film 8 is titanium silicide.

Moreover, in addition to the step (a) through (e), the following steps (f) through (h) can be included, thereby finishing fabrication of the capacitor:

(f) forming a sacrificial insulating film pattern which opens the contact plug;

(g) forming a lower electrode film on the resultant structure and performing a CMP process using the sacrificial insulating film pattern as an etch barrier to obtain a lower electrode pattern; and

(h) sequentially forming a dielectric film and an upper electrode on the resultant.

The lower electrode is a ruthenium film which is patterned by performing a CMP process using the slurry of this present invention.

A semiconductor device can be manufactured according to the method described above. The following examples are not intended to be limiting.

I. Preparation of Slurry

Example 1

CeO_2 having a grain size below 1μm was added to 10L of distilled water. Here, CeO_2 was added in a stirring speed of about 10000 rpm so that particles cannot be agglomerated. Thereafter, HNO_3 and ceric ammonium nitrate were added thereto. The resulting mixture was stirred for about 30 minutes so that it could be completely mixed and stabilized. Therefore, the slurry of the present invention was prepared. Here, CeO_2 was used in an amount of about 1% by weight of the slurry, and HNO_3 and ceric ammonium nitrate were used in an amount of about 2% by weight of the slurry, respectively.

Example 2

The procedure of Example 1 was repeated but using about 6wt% of ceric ammonium nitrate, instead of using about 2wt% of ceric ammonium nitrate.

Example 3

The procedure of Example 1 was repeated but using about 10wt% of ceric ammonium nitrate, instead of using about 2wt% of ceric ammonium nitrate.

Example 4

The procedure of Example 1 was repeated but using about 6wt% of HNO_3, instead of using about 2wt% of HNO_3.

Example 5

The procedure of Example 1 was repeated but using about 10wt% of HNO_3, instead of using about 2wt% of HNO_3.

II. CMP Process using Slurry

Example 6

A table revolution number and a wafer revolution number were respectively set up to be about 20 rpm and about 80 rpm, by using a rotary type system. Here, the CMP process was performed on the RTN thin film under a polishing pressure of about 1psi by using the slurry prepared in Example 1 (polishing speed : about 450 Å/min).

An end-point detector is used to sense a time point of exposing the interlayer insulating film.

Example 7

The procedure of Example 6 was repeated but using the slurry prepared in Example 2, instead of using the slurry prepared in Example 1 (polishing speed : about 700 Å/min).

Example 8

The procedure of Example 6 was repeated but using the slurry prepared in Example 3, instead of using the slurry prepared in Example 1 (polishing speed : about 950 Å/min).

Example 9

The procedure of Example 6 was repeated but using the slurry prepared in Example 4, instead of using the slurry prepared in Example 1 (polishing speed : about 550 Å/min).

Example 10

The procedure of Example 6 was repeated but using the slurry prepared in Example 5, instead of using the slurry prepared in Example 1 (polishing speed : about 650 Å/min).

Example 11

A table movement speed and a wafer revolution number were respectively set up to be about 500 ft/min and about 20 rpm, by using a linear type system. Here, the CMP process was performed on the RTN thin film under a polishing pressure of about 1.5psi by using the slurry prepared in Example 1 (polishing speed : about 500 Å/min).

Comparative Example 1

A table revolution number and a wafer revolution number were respectively set up to be about 20 rpm and about 80 rpm, by using a rotary type system. Here, the CMP process was performed on the RTN thin film under a polishing pressure of about 4psi by using a slurry for tungsten (SSW2000 slurry of CABOT) (polishing speed : about 350 Å/min).

Comparative Example 2

A table revolution number and a wafer revolution number were respectively set up to be about 20 rpm and about 80 rpm, by using a rotary type system. Here, the CMP process was performed on the RTN thin film under a polishing pressure of 4psi by using a slurry for aluminum (EPA5680 slurry of CABOT) (polishing speed : about 500 Å/min).

HNO_3 and ceric ammonium nitrate are added to distilled water to prepare the slurry composition. However, other additives may be further added. Moreover, HNO_3 and ceric ammonium nitrate may be added to the general slurry composition.

As discussed earlier, the CMP process is performed by using the slurry containing ceric ammonium nitrate, thereby improving the polishing speed of RTN under a low polishing pressure. In addition, the CMP process is performed according to an one-step process by using one kind of slurry. As a result, defects on the insulating film are reduced and the polishing property is improved, thereby simplifying the CMP process.

Furthermore, a process margin and a process yield are improved due to the simplified CMP process.